

UDC 666.112.2:543.42.4

IR SPECTROSCOPIC STUDY OF THE PHASE COMPOSITION FOR SODIUM SILICATE SYNTHESIZED IN AQUEOUS MEDIUM

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Translated from *Steklo i Keramika*, No. 1, pp. 6–10, January, 2007.

The distribution of components, phase composition, and structural features of sodium silicate synthesized in aqueous medium were investigated by IR spectroscopy. In prolonged storage in air, the substance partially cracked and its phase composition changed. Sodium silicates of different stoichiometry, free silica in the form of cristobalite, and sodium carbonate were the basic phases. The concentration gradients of sodium carbonate and water in the silicate in ambient conditions intensified from center to edges. Generation and development of cracks that perturbed the continuity of the synthesized substance were explained. It was noted that water sorbed from air is more dangerous for degradation of the structure than structurally bound water from the initial solution.

Sodium silicate is the main component of batches (molar content greater than 55%) for fabricating microspheres — hydrogen microcontainers. It determines the base of the phase composition of glasses and probably the phenomena during subsequent lengthy storage of the spheres related to exposure to the environment (cracking), especially of the components that cause corrosion of glass. For this reason, primary attention is always focused on phase-structure studies in chemical engineering.

We investigated the distribution of components, phase composition, and structure of sodium silicate obtained in aqueous medium by IR spectroscopy.

Very pure 10-3a silicic acid (TU 6-09-4861–80), analytically pure sodium hydroxide (GOST 4328–77), and distilled water (GOST 6709–72) were used for synthesis. A solution of sodium hydroxide and an aqueous suspension of silicic acid were prepared first. Then the alkali solution was added to the suspension while constantly stirring and heating in a MM-5 magnetic stirrer (TU 25-11.834–80) until totally dissolved. The synthesized silicate solution (0.5 liters) was quantitatively transferred to a polymer tray (230 × 100 × 25 mm) and dried for a year in air by natural evaporation of the water. A slightly opalescent substance formed as a result. Five solutions were obtained with the described scheme. These events were exactly repeated each time.

Large fragments of silicate from the near-wall and central parts and a sample of silicic acid were taken for analysis. The spectra were made on a NEXUS Fourier-transform infrared spectrometer in the diffuse reflection (DR) mode with

resolution of $4–8\text{ cm}^{-1}$ in the $400–4000\text{ cm}^{-1}$ region. A 0.01 g sample of the substance was taken on a Sartogism balance with accuracy of $\pm 0.02\text{ mg}$ and mixed with potassium bromide. Then 0.31 g of the mixture was ground for 1 min in a vibrator with grinding bodies (balls) made of steel ShKh15 (GOST 801–78). The prepared mixture was placed in a sample holder and then in a diffuse reflection module. The IR spectrum of potassium bromide powder was recorded as the background.

The wafers were also photographed, since they had external distinctive features: one wafer had unperturbed continuity while another was partially cracked, and the cracks propagated from edge to center and into the depth of the substance.

The IR spectra of the samples (Fig. 1) differed from each other, clearly indicated by the differences in their phase composition. In one case, 14 bands and in the other 18 bands are represented in Table 1 and the line spectrogram (Fig. 2).

We see from comparing the spectra (see Fig. 2) that some of the bands are in the same or in closely positioned spectral regions except for the bands with maxima at 881, 935, 987, 1463, 1645, 1694, 1705, and 3417 cm^{-1} . Another feature of the spectra is related to the intensity of the bands. The higher intensity of the bands in short-wave region 1 in the spectrum of the wafer with cracks indicates a higher water content. Both wafers were from the same whole sodium silicate fragment, i.e., we can hypothesize that favorable conditions for sorption of atmospheric water were created on the surface exhibiting the cracks. In both cases, wavelength region 4 contains very strong bands. Strong bands of medium intensity appear in region 3 at 1000 cm^{-1} . The group of bands in region 2 are weak and of medium intensity.

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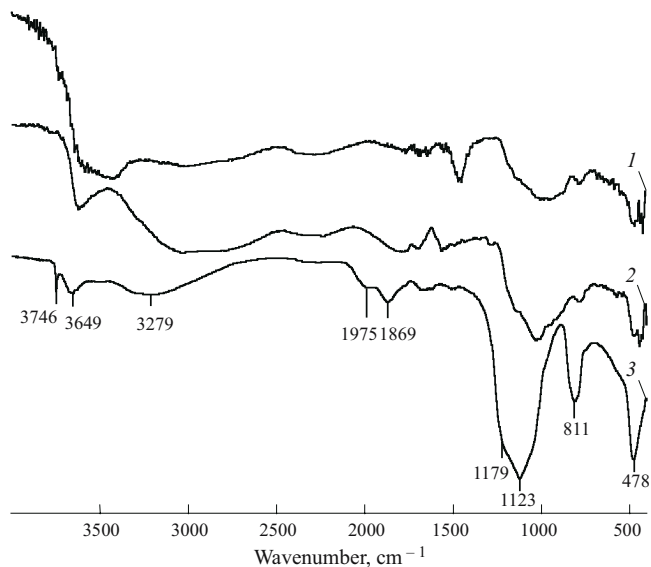
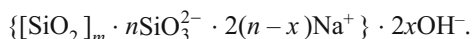
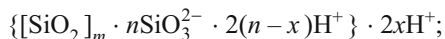


Fig. 1. IR spectra of sodium silicate with cracks (1) and without cracks (2) and silicic acid (3).

In comparison to the spectrum of pure silicic acid (see Fig. 1 and Table 1), almost all of the bands in the investigated spectra are shifted to the low-frequency region. This is due to the effect of the sodium or formation of silicates of different stoichiometry.

The sample with no cracks was taken from the central part of the dried sodium silicate. The band at 3620 cm^{-1} indicated the presence of intermicellar (molecular) water [1], which could be located in the structure of the substance. We represent the micelles of silica [2] and silica as follows:



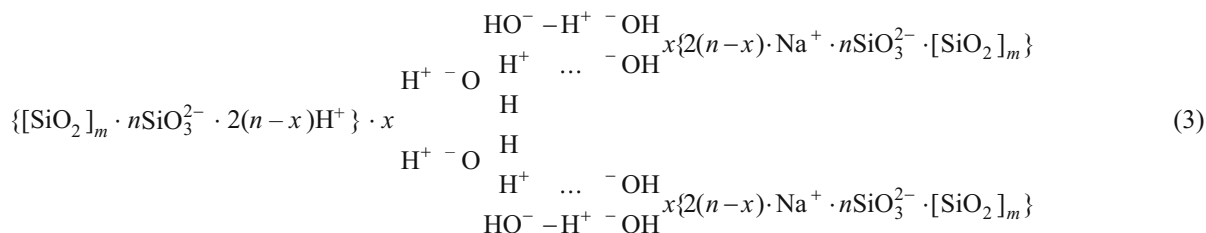
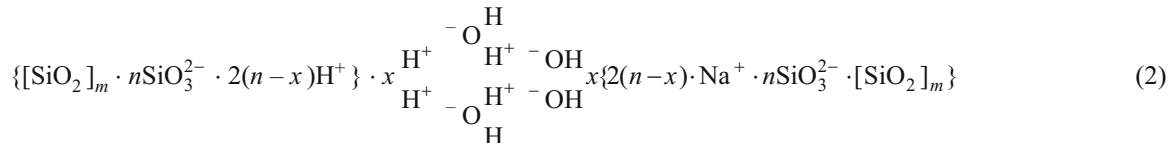
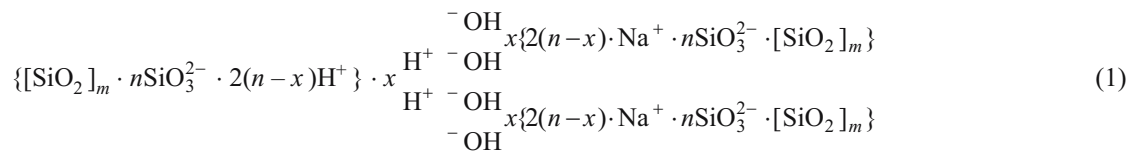
The bond between the micelles of both types is probably due to H^+ and OH^- ions and due to hydrogen bonds with molecules of water:

TABLE 1

Wafer with no cracks		Wafers with cracks		Silicic acid	
wave-number, cm^{-1}	intensity, %	wave-number, cm^{-1}	intensity, %	wave-number, cm^{-1}	intensity, %
444	100.00 v.s.	440	95.35 v.s.	—	—
477	93.20 v.s.	475	100.00 v.s.	478	91 v.s.
776	71.43 s.	779	51.16 m.	810	65 s.
—	—	881	62.79 s.	—	—
916	83.67 s.	—	—	—	—
—	—	935	69.77 s.	—	—
947	87.76 s.	948	69.77 s.	—	—
968	89.12 s.	960	69.77 s.	993	49 m.
—	—	987	69.77 s.	—	—
1008	95.92 v.s.	1008	69.77 s.	—	—
1032	97.28 v.s.	1030	67.44 s.	—	—
1138	78.23 s.	1133	46.51 m.	1123	100 v.s.
—	—	—	—	1179	91 v.s.
1284	37.41 m.	—	—	—	—
—	—	1463	48.84 m.	—	—
1564 m.	40.14 m.	1554	16.28 w.	—	—
—	—	1645	20.93 w.	1670	14 w.
1705 m.	38.78 m.	1694	20.93 w.	—	—
1777 m.	41.50 m.	1769	16.28 w.	—	—
—	—	—	—	1869	20 w.
—	—	—	—	1975	14 w.
—	—	3417	46.51 m.	—	—
3620 w.	14.29 w.	3623	25.58 w.	3649	17 w.
—	—	—	—	3746	10 w.

Note: v.s.) very strong; s.) strong; m.) medium; w.) weak; bands corresponding to the bands in the spectrum of sodium silicate are reported in the spectrum of the acid.

The band with a maximum at 3620 cm^{-1} belongs to antiphase vibrations of conjugated OH groups [3] with which curved chains — schemes (1) and (3) — and cyclic frag-



ments in the form of isolated “islands” — scheme (2) — can be formed.

The band in the given region indicates the well-formed structure of the substance and inclusion of water directly in its structure — scheme (1). There is most likely no water in the free state. Molecular water in the form of dipoles — the central part of schemes (2) and (3) — binds micelles similar to bridges. We can hypothesize that in the area of contact of micelles with air, hydrogen bonds break when the pressure over the silicate drops, polarization of the dipoles is removed, and molecules of water become mobile and leave the substance, passing into the gas phase above its surface. The defect that appears in this way initiates a crack. Scheme (1) is less probable for explaining cracking, since direct bonds between H^+ and HO^- ions are stronger than the same bonds separated by water dipoles.

The band with a maximum at 1777 cm^{-1} is perhaps due to vibrations of the atoms in a $>C=O$ bond [4], i.e., an organic impurity could be present in the silicate solution. They were especially not used for synthesis of the silicate. However, the distilled water used as a solvent was stored in a polymer container before synthesis began. Some organic substances (plastic fillers, polymerization catalysts, etc.) perhaps partially migrated into the water.

The band with a maximum at 1705 cm^{-1} indicates formation of chains with structural fragments bound by hydroxyl bridges [5] — schemes (1) and (3). The appearance of a band with a maximum at 1564 cm^{-1} in the spectrum is perhaps due to vibrations of the atoms in the $C-O$ bond in the carbonate Na_2CO_3 [6]. The band with a maximum at 1284 cm^{-1} indicates deformation vibrations of the $\equiv Si-OH$ bond [5]. The band of stretching vibrations with a maximum at 1705 cm^{-1} can be considered an indicator of formation of hydrated sodium silicates of chain structure [5].

The glass-forming composition was calculated with consideration of the silicate ratio, $n_{Si} = 3$, so that not all of the silicic acid could participate in silicate formation. The bands with maxima at $1008-1138\text{ cm}^{-1}$ and the absence of a band with a maximum at 500 cm^{-1} confirm the presence of residual three-dimensional fragments of silica structure bound by $O-Si-O$ oxygen bridges [7].

The band with a maximum at 1032 cm^{-1} can be assigned to vibrations of atoms in the bonds of silicates from $Na_2O \cdot SiO_2$ to $Na_2O \cdot 3SiO_2$ [6] with well-formed crystal lattices (strong band with a sharp peak).

The band with a maximum at 968 cm^{-1} is difficult to unambiguously identify, since it could be due to both stretching vibrations of the atoms in the $Si-O$ bond in $Na_2O \cdot 2SiO_2$ and to deformation vibrations of the atoms in a $O-C-O$ bond [6, 8], so that it could indicate formation of a carbonate phase together with the band of stretching vibrations in the 1564 cm^{-1} region. At the same time, the doublet (strong bands with maxima at $968-947\text{ cm}^{-1}$) indicates the silicate phase; the second band is located in a region of the spectrum characteristic of high-silica silicates.

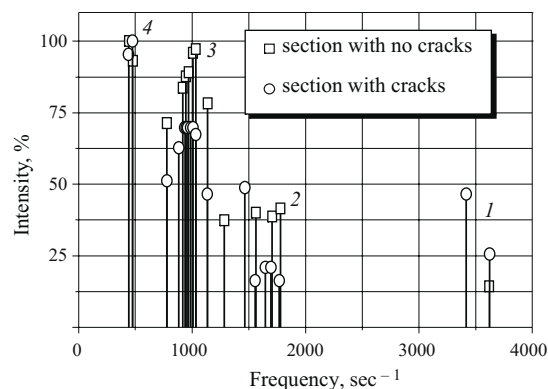


Fig. 2. Line spectrogram of sodium silica: 1–4) regions of the spectra.

The band with a maximum at 916 cm^{-1} is caused by asymmetric vibrations of the $Si-O$ bond [1] in silicates from $2Na_2O \cdot SiO_2$ to $3Na_2O \cdot SiO_2$ [6]. The strong band with a maximum at 776 cm^{-1} could indicate the presence of cristobalite with a well-formed crystal lattice [1]. There were probably also other modifications of silica, since at least another six weakly resolved bands in the form of shoulders can be distinguished in the overall contour. The very strong bands with maxima at 477 and 444 cm^{-1} indicate [1] a well-formed crystalline phase of silica in tetrahedral coordination with respect to $[SiO_4]$ oxygen; the tetrahedrons bound by oxygen bridges form a structural motif of the skeleton type.

The sample with cracks was taken from the part of the sodium silicate adjoining the walls of the drying tray.

In comparing the spectra (see Fig. 1), note that the crystalline phases are more pronounced in the wafers with no cracks than in the wafers with cracks (almost all of the bands in their spectrum are diffuse and less intense). This can be explained as follows. In cracking, the contact area of the silica with atmospheric moisture increased significantly, but water was present on the surface of fresh cracks in the form of OH groups in $\equiv Si-OH$ silanol groups, confirmed by the bands with maxima at 3623 and 881 cm^{-1} (the latter in the spectrum of wafers with no cracks is represented as a very weak shoulder) [3, 9].

The silanol groups subsequently reacted with molecules of atmospheric water and as a result, a film of “liquid” water was created on the surface (the surface felt greasy). This is indicated by the strong band in the spectrum with a maximum at 3417 cm^{-1} and the band with a maximum at 1645 cm^{-1} , while there were no bands in the region of 3740 cm^{-1} [10, 11]. The band with a maximum at 1694 cm^{-1} also confirms the presence of molecular water [7]. Penetrating the mouths of the cracks, the “liquid” water split them and intensified growth. In addition, the layer of water on the surface facilitated absorption of CO_2 from the air, causing corrosion of the sodium silicate as a result of formation of sodium carbonate. The strong band with a maxi-

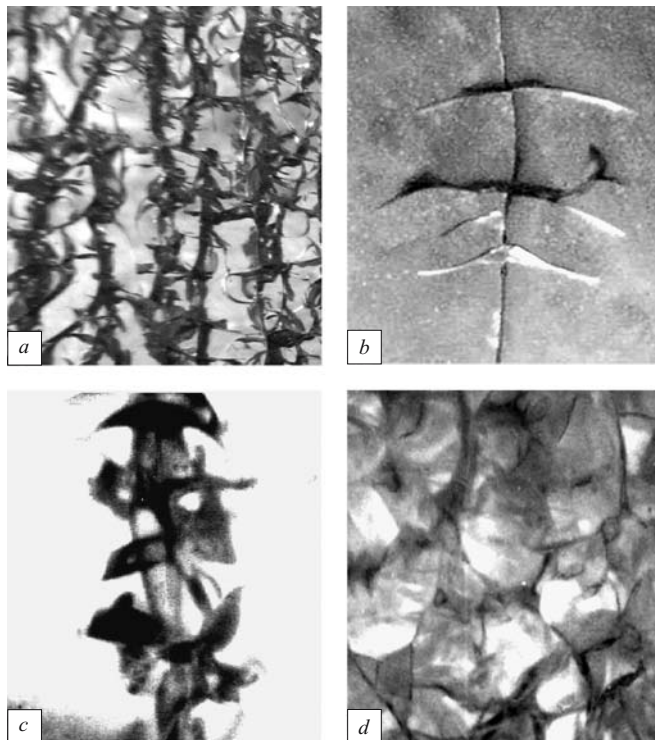


Fig. 3. Development of cracks in sodium silicate: *a*) longitudinal channels with side branches; *b*) same at magnification by 2 times; *c*) individually positioned cracks with incipient side branches ($\times 56$); *d*) fragments of the substance after joining of the side branches of the main cracks.

mum at 1463 cm^{-1} in the spectrum of the wafers with cracks indicates this [7].

At the beginning of drying, the cracks were relatively straight and short. In 1–2 days, they increased in length and side branches appeared and grew toward each other (Fig. 3*a* and *b*). Some of the side branches grew from the initial main crack to join with the side branches of neighboring main cracks, so that round fragments of the substance were formed (see Fig. 3*b*). If external processes are a reflection of internal processes, it is logical to hypothesize that this type of breakdown was caused by separation of micelles on removal of molecular water and indicated the existence of cyclic structural motifs in the sodium silicate. This is confirmed by the presence of a band in the spectrum with a maximum at 3623 cm^{-1} .

The intermicellar water was not eliminated in the form of a liquid (it did not flow out) but in the form of vapor. In passing into the gas state, its volume naturally increased and the channels along which the vapor went out into the atmosphere became tubular in shape, since the substance still retained elasticity. Note in Fig. 3*c* that the main crack surrounded by side branches has the shape characteristic of hollow bodies (the “fuzziness” of the image is due to the fact that the crack was in the thickness of the sodium silicate). The appearance of side branches caused dissipation of the energy of the main

cracks and growth was inhibited. With no external mechanical effects, the main cracks could not totally destroy the substance for a relatively short time. Breakdown took place gradually. From April, 2004 to March, 2006, the silicate was not totally covered by a network of cracks and there were continuous sections in the central part. We thus attribute the appearance and development of cracks to elimination of intermicellar water.

Considering the synthesized sodium silicate as a model of glass, we note the following. Since humidity is subject to seasonal fluctuations, the water content in the glass cannot remain constant. As a result of this, a network of cracks is formed in the surface and near-surface layers of the substance and a carbonate deposit appears. After preparation, silicate microspheres should be stored in a protected atmosphere or in a medium with a moisture content no lower than the moisture content of the glass. The second version is preferable, since microspheres taken from the container for storage are less subject to ambient humidity drops, and this means that they will crack to a lesser degree.

The band with a maximum at 1554 cm^{-1} in the broad band with a complex outline is most probably assigned to vibrations of the $>\text{C}=\text{O}$ group in organic substance [9]. The band is weakly resolved, so that the substance was present as an impurity.

Bands [6] indicating formation of three-dimensional structural motifs due to apical joining of $[\text{SiO}_4]$ tetrahedrons are usually observed in the region of $1134\text{--}881\text{ cm}^{-1}$. However, in the spectrum of the wafers with cracks, the peak is broadened and diffuse. For this reason, we can hypothesize that the three-dimensional motif in them is less extensive than in the wafers with no cracks, and there are more ruptures of $\text{O}-\text{Si}-\text{O}$ bonds and $\equiv\text{Si}-\text{O}-\text{Na}$ groups in the wafers with cracks [6]. The band with a maximum at 987 cm^{-1} [6] is probably due to stretching vibrations of the $\text{Si}-\text{O}$ bond in $[\text{SiO}_4]$ tetrahedrons. The band with a maximum at 935 cm^{-1} indicates formation of alkaline silicate. The fuzziness of the spectrum at $1134\text{--}881\text{ cm}^{-1}$ indicates the absence of distinct boundaries between the three-dimensional fragments and the island structure, i.e., the formation of an intermediate region between highly polymerized motifs with a high proportion of covalent bonds and one-dimensional isolated complexes [6] — scheme (2).

The interpretation of the unexamined bands in the spectrum of the wafers with cracks but corresponding in position to the bands in the spectrum of wafers without cracks holds.

As a result of studying sodium silicate obtained in aqueous medium by IR spectroscopy, we note that the synthetic substance had a well-formed crystal structure represented by island, chain, and three-dimensional motifs. In the structure of the substance, molecular water played the role of bridges between the individual micelles. In addition, it could also be represented in molecular form in the composition of crystal hydrates and in the form of hydroxyl groups in silanol groups. It is not possible to unambiguously state that

hydroxyl groups bound structural fragments, since this could be nonbridge bonds directed inside the pores formed and groups positioned in the surface layer on the boundary of contact with air.

The phase composition is represented by sodium silicates of different stoichiometry, residual free silica in the form of cristobalite, and sodium carbonate, and organic substance was present as impurity. In prolonged presence in ambient conditions, the concentration gradient of sodium carbonate and water in the sodium silicate strengthened in the direction from center to edges, where crack formation began. Water sorbed from air is more dangerous than structurally bound water from the initial solution with respect to degradation of the substance.

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